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Direct Determination of Oxygen in the Organic Compounds by the Hydrogenation. I. Search of the Optimum Analytical Conditions.

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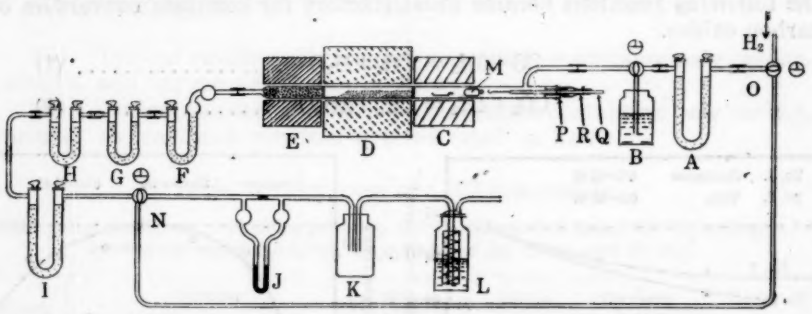
The direct determination of oxygen in the organic compounds by the hydrogenation method according to Meulen[1] was examined in details. Inaba and Abe[2] succeeded in the analysis of saccharose which was considered to be a difficult one. W. R. Kirner,[3] however, could not obtain good results with saccharose and he discussed the problem of application of corrections obtained in the blank experiments. We, therefore, hoped to reexamine and clear up these points by experiments and also by theoretical consideration of this hydrogenation method.

Experimental Details. (1) *The apparatus* used is shown in Fig. 1. It is essentially the same as Russel and Fullton's[4] apparatus.



A: $CaCl_2$ or NaOH granules
B: Conc. H_2SO_4
C: Sample heating furnace
D: Cracking furnace
E: Reduction furnace
F, G, H: $CaCl_2$ or NaOH granules
I: $CaCl_2$ tube
J: Flowmeter
K: Empty bottle
L: Conc. H_2SO_4
M: Quartz plag
N: Three way cock
O: Three way cock
P: Rubber stopper
Q: Glass tube
R: Rubber tube

Fig. 1. Apparatus.

(1) H. Meulen: *Rec. trav. chim.*, **53** (1934), 118; *Bull. Soc. Chim.*, [5] **2** (1935), 1692.
(2) T. Inaba and R. Abe: *J. Soc. Chem. Ind., Japan*, **39**, 91 B (1936).
(3) W. R. Kirner: *Ind. Eng, Chem., Anal. Ed.*, **9** (1937), 535–539.
(4) W. W. Russel, J. W. Fullton: *Ind. Eng. Chem., Anal. Ed.*, **5** (1933), 384.

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(2) *The catalyst*: The cracking (Pt-silica gel) and reducing (Ni-thoria) catalysts were prepared according to Russel's procedure[4]. The latter was reduced with hydrogen at 350°C. for 3 hours and then at 500°C. for 12~15 hours, thereby the water formed by reduction of catalyst would be less than one mg. per hour. After 7–10 analyses the Pt-silica gel catalyst was covered with free carbon deposit and lost its activity and, therefore, it was required to revive it by burning the carbon deposit with streaming air.

(3) *The analytical procedure* was essentially the same as Inaba and Abe's.[2]

(4) *The absorbent*: Calcium chloride was used for typical substances which contained only carbon, hydrogen and oxygen, and caustic soda or soda lime, for nitrogen containing samples, the latter was preliminarily treated with dried ammonia gas.

(5) *The samples* were all Merck's preparations and were dried on phosphorus pentoxide in the Abderhalden vacuum drying apparatus.

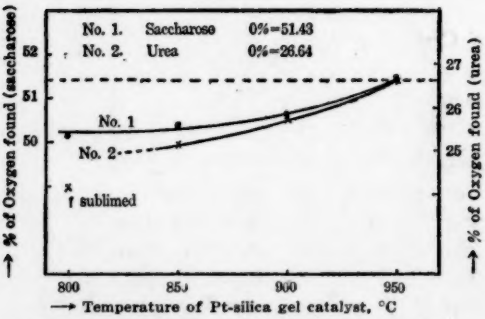
Experimental Results. The optimum analytical conditions were searched with saccharose and the results obtained were given in Fig. 2–5.

(1) *Cracking temperature*: Under 950°C. the analyses gave lower results, indicating the incomplete cracking of organic vapours (Fig. 2).

(2) *Reducing temperature*: The temperature around 350°C. was found to be satisfactory (Fig. 3). Under 300°C. the reducing velocity on Ni-catalyst was too slow and above 400°C. the equilibrium conditions of the following reactions became unsatisfactory for complete conversion of carbon oxides.

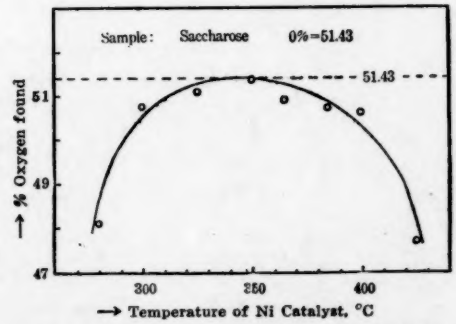
$$CO+3H_2=CH_4+H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$CO_2+4H_2=CH_4+2H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$



Analytical conditions: Temp. of Ni catalyst 350 C; hydrogen streaming velocity 5 l/hr; analytical time, saccharose 60 min., urea 80 min.

Fig. 2. Influence of Temperature of Pt-silica Gel Catalyst.



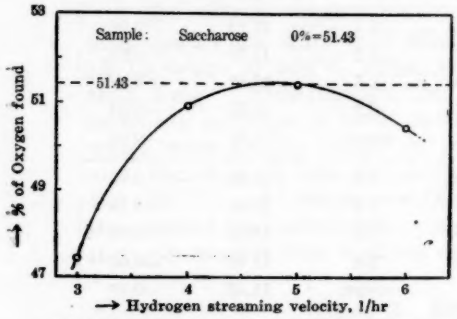
Analytical conditions: Temp. of Pt-silica gel catalyst 950 C; hydrogen streaming velocity 5 l/hr; analytical time 60 min.

Fig. 3. Relation between Reduction Temperatures and % of Oxygen found.

(3) *Streaming velocity of hydrogen*: Around 5 l./hr. was found to be best suited (Fig. 4). When the hydrogen streamed too slowly the

vapour pressure of carbon oxides became too high and, therefore, equilibrium conditions of reaction (1) and (2) became unfavourable for the analytical purpose.

(4) *Amount of sample taken*: The optimum amount of sample to be taken were investigated, and the product of the weight (in gram) and the oxygen content (in percentage) of the sample taken was expressed as K. Only when K was below 12, saccharose and urea gave good results as shown in Fig. 5.



Analytical conditions: Temp. of Pt-silica gel catalyst 950 C: temp. of Ni catalyst 350°C; analytical time 60 min.

Fig. 4. Influence of Hydrogen Streaming Velocity.

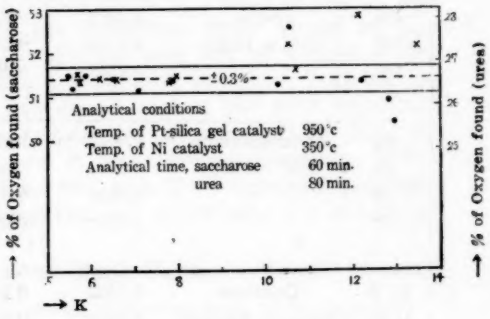


Fig. 5. Influence of weight of sample.

(5) Typical results with several compounds containing only carbon, hydrogen, and oxygen are shown in Table 1.

(6) Typical results with several compounds containing only carbon, hydrogen, oxygen, and nitrogen are indicated in Table 2.

Table 1. Analyses of CHO compounds.

Analytical conditions: Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., time required for these runs 60 min.

Expt. No.	Sample		Water obtained g.	Blank value mg.	Oxygen found %	Error %
	Kinds	Wt. g.				
58		0.1070	0.0642	2.2	51.50	+0.07
57	Saccharose	0.1121	0.0670	2.2	51.34	−0.09
25		0.1152	0.0688	2.0	51.50	+0.07
56	(0% = 51.43)	0.1282	0.0772	3.0	51.40	−0.03
24		0.1537	0.0912	2.2	51.42	−0.01
				mean	51.43	+0
78	Benzoic	0.0869	0.0265	0.8	26.26	+0.04
94	Acid	0.1000	0.0315	1.7	26.46	+0.24
76	(0% = 26.22)	0.1144	0.0346	0.8	26.32	+0.10
92		0.1153	0.0354	1.7	25.96	−0.26
				mean	26.25	+0.03

Table 1.—(*Concluded*)

Expt. No.	Sample Kinds	Wt. g.	Water obtained g.	Blank value mg.	Oxygen found %	Error %
67	α-Naphthalic Acid (0% = 18.60)	0.1002	0.0237	3.5	18.52	−0.08
97	β-Naphthalic	0.0752	0.0174	1.7	18.54	−0.06
105	Acid	0.1027	0.0237	2.2	18.59	−0.01
104	(0% = 18.60)	0.1113	0.0259	2.5	18.67	+0.07
106		0.1148	0.0262	2.2	18.56	−0.04
				mean	18.58	−0.02
63	Anthraquinone	0.0642	0.0129	1.8	15.36	+0.02
64	(0% = 15.38)	0.0799	0.0163	2.2	15.56	+0.18
65		0.0993	0.0196	2.2	15.56	+0.18
62		0.1163	0.0222	2.0	15.43	+0.05
				mean	15.48	+0.10
C- 9	Cellulose	0.1932	0.1069	3.1	49.88	−0.29
C-10	(indirect method)	0.2441	0.1403	2.1	50.28	+0.11
	(0% = 50.17)			mean	50.08	−0.09

Table 2. Analyses of CHON compounds.

Analytical condition: Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l./hr., time required for these runs 80~90 min.

Expt. No.	Sample Kinds	Wt. g.	Water obtained g.	Blank value mg.	Oxygen found %	Error %	Absorbent
116	Urea (0% = 26.64)	0.1147	0.0355	2.0	26.71	+0.07	Granules of caustic soda
119		0.1325	0.0416	2.0	26.54	−0.10	,,
118		0.1329	0.0422	2.0	26.84	+0.22	,,
117		0.1478	0.0434	2.0	26.68	+0.04	,,
135		0.2252	0.0688	1.3	26.62	−0.02	Soda lime
136		0.2446	0.0750	1.3	26.79	+0.15	,,
				mean	26.70	+0.06	
121	Dimethyl-glyoxime (0% = 27.57)	0.0809	0.0258	2.0	27.77	+0.20	Granules of caustic soda
140		0.1170	0.0383	2.0	27.88	+0.31	Soda lime
139		0.1198	0.0396	2.0	27.55	−0.02	,,
				mean	27.73	+0.16	
L-3	Beech-Lignin (indirect method) (0% = 30.66)	0.1234	0.0423	0.1	30.47	−0.19	Granules of caustic soda
L-6		0.1432	0.0500	0.9	30.51	−0.15	,,
				mean	30.49	−0.17	

Discussion of Results. (1) *Analysis of saccharose*: W. R. Kirner[3] was inclined to believe that saccharose left much carbon residues which retained some oxygen very tenaciously and thus gave lower values than the calculated ones. Russel, Fullton[4] and Inaba, Abe[2] and the authors all employed Pt-silica gel catalyst for the cracking purpose and they all obtained good results with saccharose. As made clear above there is an optimum range in every analytical condition and, therefore, one mistake in selecting these ranges would bring unsatisfactory results.

(2) *Blank experiments*: The reduction of Ni-thoria catalyst prepared by the ignition of mixed nitrates requires 3 days at 400°C. and 12–15 hours at 500°C. after which the reduction water would be less than 1 mg.. Even though the catalyst tube was left overnight under hydrogen pressure, a little above the atmospheric pressure, 7–16 mg. of water were always caught in the first blank run of the next morning, and, therefore, it was necessary to reduce the catalyst half an hour at 450~500°C. and to make one blank run at 350°C. every morning. When the catalyst was sufficiently reduced for use, and if we streamed hydrogen through catalyst tube without opening the end of the tube for 1 hour at

Table 3. Effects of Blank Value.

Analytical condition: Pt-silica gel temp. 950°C., Ni-catalyst temp. 350°C., hydrogen streaming velocity 5 l/hr., time required for these runs 60 min.

Expt. No.	Analytical order	Sample		Water obtained g.	Blank value mg.	Oxygen found %	Error %	Note
		Kinds	Wt. g.					
(1) Case in which the Ni-catalyst was not yet completely reduced								
55	1	Saccharose	0.1089	0.0659	3.5	51.19	−0.24	
56	2	(0% = 51.43)	0.1282	0.0772	3.0	51.40	−0.03	
57	3		0.1121	0.0670	2.2	51.34	−0.09	
58	4		0.1072	0.0642	2.2	51.50	+0.07	
104	1	β-Naphthalic	0.1113	0.0259	2.5	18.67	+0.07	
105	2	Acid	0.1027	0.0237	2.2	18.59	−0.01	
106	3	(0% = 18.60)	0.1148	0.0262	2.2	18.56	−0.04	
(2) Cases in which the Ni-catalyst was almost completely reduced								
75	1	Benzoic	0.0913	0.0259	0.6	24.61	−1.61	too low
76	2	Acid	0.1144	0.0346	0.6	26.39	+0.17	
77	3	(0% = 26.22)	0.0869	0.0264	0.6	26.35	+0.12	
86	1	Saccharose	0.1042	0.0610	1.7	50.55	−0.88	too low
87	2	(0% = 51.43)	0.2007	0.1176	1.7	51.29	−0.14	
88	3		0.2510	0.1442	1.7	50.42	−1.01	sample excess (K = 12.9)
89	1	Saccharose	0.2147	0.1241	1.6	50.67	−0.76	too low
90	2	(0% = 5143)	0.2449	0.1450	1.6	50.96	−0.47	sample excess (K = 12.8)
91	3		0.2211	0.1295	1.6	51.37	−0.06	

the rate of 5 l./hr., we would obtain about 1 mg./hr. of water. If, however, we followed the procedure just as in the actual analysis, that is, opening the end of the tube and streaming out the air in the reverse direction for 10 minutes, we always obtained about 2–3 mg./hr. of water. Strictly speaking we should apply these values to the analysis as corrections of the blank experiments, and so we have adopted this way of correction throughout this paper and obtained satisfactory results.

When the Ni-catalyst was reduced completely, the blank water value would be 0.6~1.7 mg./hr. and in these cases the first run used to give somewhat low results as clearly shown in Table 3. This means that the over-dried catalyst surface retained very tenaciously some water produced during the analysis and therefore, did not recover the original surface conditions within the limited experimental period. Thus we should make three successive runs of which the first might be looked upon as preliminary and the last as the check.

(3) In this hydrogenation analysis the sample should be very slowly vaporized or cracked so as not to cause a rapid decomposition of the sample, accordingly not to raise too high the partial pressure of carbon monoxide or carbon dioxide; otherwise the reduction equilibrium of reaction (1) or (2) becomes unfavourable for the complete reduction of carbon oxides and would give the analyses low results. From these standpoints we should make the preliminary run and should find the suitable heating rate for unknown sample to be analysed. These points will be discussed in details in the next paper.

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Studies on the Derivatives of Biphenylene Oxide. V. Bromo-derivatives of Biphenylene Oxide.

By Seishi YAMASHIRO.

(Received November 24, 1940.)

Among the bromo-derivatives of biphenylene oxide, although all isomers of the monobromo-compounds and three dibromo-compounds (2,3-,[1] 2,6-[2] and 3,6[3]-dibromobiphenylene oxides) are already prepared by many investigators, yet nothing has been reported to this day about the tri- and tetra-bromo compounds.

(1) K. Tatematsu and B. Kubota, this Bulletin, **9** (1934), 456.
(2) H. McCombie, W. G. Macmillan and H. A. Scarborough, *J. Chem. Soc.*, **1913**, 536.
(3) O. Hoffmeister, *Ann.*, **159** (1871), 215; H. McCombie, W. G. Macmillan and H. A. Scarborough, *J. Chem. Soc.*, **1913**, 536; N. M. Cullinane, H. G. Davey and H. J. H. Padfield, *J. Chem. Soc.*, **1934**, 719; H. Gilman, H. B. Willis and J. Swislowsky, *J. Am. Chem. Soc.*, **61** (1939), 1372.

The present author obtained recently one tribromo- and two tetrabromo-biphenylene oxides, by isolating them from the bromination products of 3,6-dibromobiphenylene oxide. He inferred, from his experiment on the nitration of 3,6-dinitrobiphenylene oxide, that each of these newly obtained compounds might be respectively 2,3,6-tri- and 1,3,6,7- and 2,3,6,7-tetra-bromo compounds (I, II and III), because in that experiment 3,6-dinitrobiphenylene oxide gave mainly the 2,3,6-trinitro-compound (together with the 1,3,6-trinitro-compound by the bye) which converted into 1,3,6,7- and 2,3,6,7-tetranitrobiphenylene oxides. In order to confirm this inferrence, the bromination of biphenylene oxide and its bromo derivatives was again examined systematically, and in that experiment a new dibromobiphenylene oxide was also obtained. Its result may be described here in order.

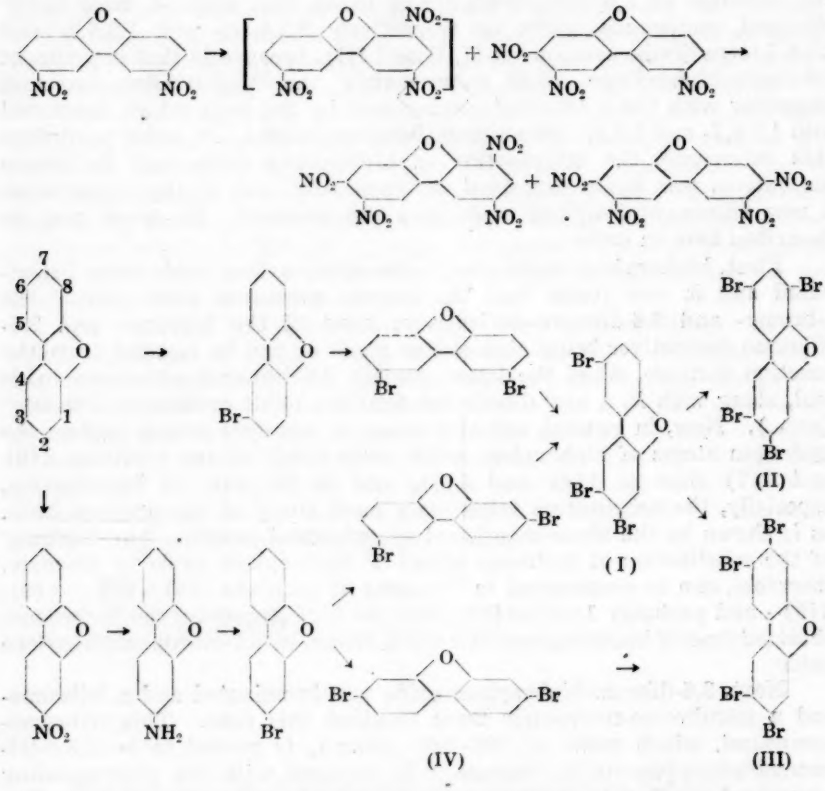
First, biphenylene oxide and 2-bromobiphenylene oxide were brominated and it was found that the former substance gives mainly the 3-bromo- and 3,6-dibromo-derivatives; none of the 2-bromo- and 2,6-dibromo derivatives being obtained so much as can be isolated from the reaction mixture, while the latter, mainly 2,6-dibromobiphenylene oxide and, along with it, a new dibromobiphenylene oxide melting at 199–200° (corr.). Now, in general, negative atoms or negative groups replace the hydrogen atoms of biphenylene oxide more freely at the positions 3(6) and 2(7) than at 1(8) and 4(5), and in the case of bromination, especially, the substitution takes place most freely at the position 3(6), as is shown by the above-mentioned experimental results. The tendency of the substitution of hydrogen atoms of biphenylene oxide by bromine, therefore, can be represented in the order of positions $3(6)>2(7)>1(8)$, $4(5)-$ and probably $1(8)>4(5)-$, and, as a consequence, the by-product obtained from 2-bromobiphenylene oxide should be 2,7-dibromobiphenylene oxide.

Next, 3,6-dibromobiphenylene oxide was brominated and a tribromo- and a tetrabromo-compounds were obtained this time. This tribromo-compound, which melts at 202–203° (corr.), is proved to be 2,3,6-tribromobiphenylene oxide, because it is identical with the corresponding compound which was obtained from 2,6-dibromobiphenylene oxide. The last compound gave on bromination two tetrabromo compounds besides the 2,3,6-tribromo-compound. The tetrabromo compounds isolated in these experiments are identical with the corresponding compounds which can be obtained from 2,3,6-tribromobiphenylene oxide.

When 2,3,6-tribromobiphenylene oxide was brominated, it converted into two tetrabromo-compounds, one of which, melting at 306–307° (corr.), is the main product, while the other meltitng at 248–249° (corr.), a by-product. Judging from this experimental result and the above-mentioned tendency of the substitution by bromine, it is rather reasonable to conclude that the higher melting one is 2,3,6,7-tetrabromobiphenylene oxide, and the lower, 1,3,6,7-tetrabromobiphenylene oxide. Further support for this conclusion can be found in the result of bromination of the 2,7-dibromo-compound mentioned above, because this compound converts into a tetrabromo-compound which is identical with the higher melting tetrabromobiphenylene oxide.

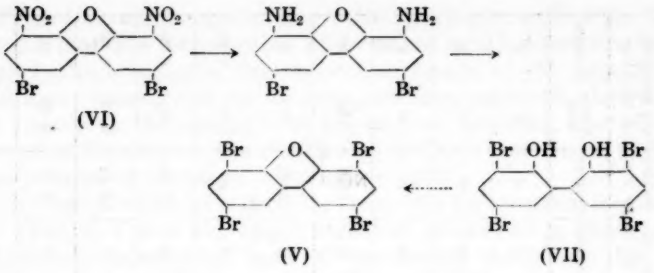
In summary, the processes of the reactions, which were utilized to

establish the constitutions of the new bromo derivatives of biphenylene oxide, therefore, may be represented by the following schemes:



For the purpose of comparing with one another the possible isomers of the tetrabromobiphenylene oxides which would be found in the bromination products of 3,6-dibromobiphenylene oxide, 1,3,6,8-tetrabromobiphenylene oxide (V) was prepared from 3,6-dibromo-1,8-dinitrobiphenylene oxide (VI) which will be described in Part VII. The process of the reactions in that case is represented by the real-lined arrows in the scheme shown below. It was tried in vain, however, to prepare the same tetrabromo compound from 3,3′,5,5′-tetrabromo-2,2′-dihydroxydiphenyl (VII) by heating it in a sealed tube, for 5 hours at about 195–200°, in the presence of hydrobromic acid and a small quantity of red phosphorus, or by melting its acetyl derivative in mixing with dry carbonate of sodium or of barium.

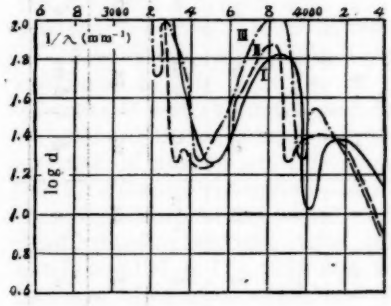
The physical properties and the absorption curves of biphenylene oxide and its bromo-derivatives were compared as in Table 1 and Figs. 1–4, which will be utilized for the benefit of isolation and identification of these compounds.



(VI)

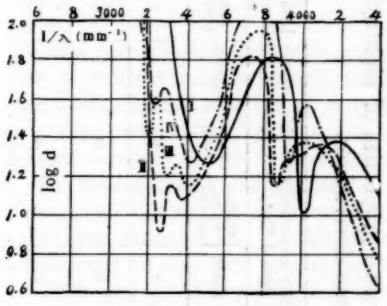
(V) (VII)

Comparison of the absorption curves of biphenylene oxide and its bromo derivatives.



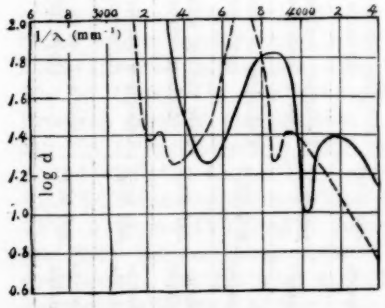
I (——) Biphenylene oxide.
II (– – –) 2-Bromobiphenylene oxide.
III (–·–) 3-Bromobiphenylene oxide.

Fig. 1. Monobromobiphenylene oxides, M/10000 alcoholic solutions.



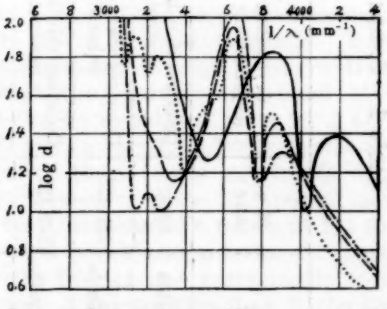
I (——) Biphenylene oxide.
II (– – –) 2,7-Dibromobiphenylene oxide.
III (····) 2,6-Dibromobiphenylene oxide.
IV (–·–) 3,6-Dibromobiphenylene oxide.

Fig. 2. Dibromobiphenylene oxides, M/10000 alcoholic solutions.



I (——) Biphenylene oxide.
II (– – –) 2,3,6-Tribromobiphenylene oxide.

Fig. 3. Tribromobiphenylene oxide, M/10000 alcoholic solution.



I (——) Biphenylene oxide.
II (– – –) 1,3,6,7-Tetrabromobiphenylene oxide.
III (····) 1,3,6,8-Tetrabromo- ,, ,,
IV (–·–) 2,3,6,7-Tetrabromo- ,, ,,

Fig. 4. Tetrabromobiphenylene oxides, M/10000 alcoholic solutions.

Table 1. Comparison of the physical properties of biphenylene oxide and its bromo derivatives.

Compound	M.p. (corr.)	Crystalline form (crystallizing solvent)	Solubility (e: easily soluble, e-m: less easily soluble, m: moderately soluble, d-m: less difficultly soluble, d: difficultly soluble; e > e-m > m > d-m > d.)										
			Ligroin	Ether	Carbon tetrachloride	Chloroform	Benzene	Ethyl acetate	Methanol	Ethanol	Acetone	Acetic acid	Toluene
Biphenylene oxide	86–87°	Colorless thin blades (ethanol)	e	e	e	e	e	e	e	e	e	e	e
2-Bromobiphenylene oxide	121–122°	Colorless hexagonal plates (ethanol)	e	e	e	e	e	e	m	m	e	e	e
3-Bromobiphenylene oxide	109–110°	Colorless thin blades (ethanol)	m	e	e	e	e	e	m	m	e	e	e
2,6-Dibromobiphenylene oxide	178–179°	Colorless needles (acetone)	d	e-m	e	e	e	e	d	d	e-m	m	e
2,7-Dibromobiphenylene oxide	199–200°	Colorless needles (acetone)	d	e-m	e	e	e	e	d	d	e-m	m	e
3,6-Dibromobiphenylene oxide	199–200°	Colorless rectangular plates (acetic acid)	d	m	e	e	e-m	e	d	d	e	m	e-m
2,3,6-Tribromobiphenylene oxide	202–203°	Colorless needles (acetone)	d	d	m	m	e-m	m	d	d	d m	d	e-m
1,3,6,8-Tetrabromobiphenylene oxide	237–238°	Pale yellow small needles (carbon tetrachloride)	d	d	e-m	e-m	e-m	e-m	d	d	d-m	d-m	e m
1,3,6,7-Tetrabromobiphenylene oxide	248–249°	Colorless needles (toluene)	d	d	m	m	m	d-m	d	d	d-m	d-m	m
2,3,6,7-Tetrabromobiphenylene oxide	306–307°	Colorless large needles (toluene)	d	d	d	d	d-m	d	d	d	d	d	m

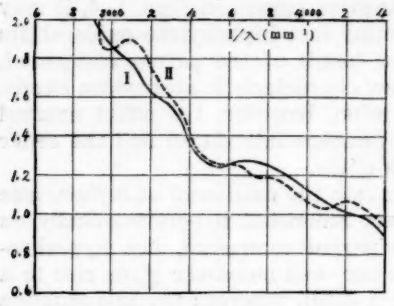
From the comparison of these absorption curves in Figs. 1–4, it may be found that the introduction of bromine into biphenylene oxide shifts always bathochromically the absorption bands of the parent compound, and in many cases gives rise to some new characteristic absorption bands. With regard to the strength of absorption, however, the effect exerted by bromine depends on the position of bromine introduced and the order of the absorption bands of biphenylene oxide.

The introduction of a bromine atom into the position 2 of biphenylene oxide (Fig. 1, Curve II) exerts an effect somewhat hyperchromically on the first less refrangible band of the parent compound, but hypochromically on the second more refrangible one, and moreover gives rise to a small characteristic band at $1/\lambda$ (mm^{-1}) 4330, whereas the introduction of a bromine atom into the position 3 (Fig. 1, Curve III) exerts no effect upon the strength of absorption in the first band of the parent compound, but it shows a hypochromic effect on the second one and moreover gives rise to a selective absorption band at 3220.

Among the absorption spectra of the dibromobiphenylene oxides compared in Fig. 2, those of 2,7- and 3,6-dibromobiphenylene oxides (Curves II and IV) have each three bands which are similar to a series of bands of 2- and 3-bromobiphenylene oxides respectively except for the strength of absorption, this being increased—especially so in the case of the 2,7-dibromo-compound—owing to the symmetrical constitutions of these two dibromo compounds; on the contrary, that of the unsymmetrical 2,6-dibromobiphenylene oxide (Curve III) has four bands, of which the bands located at $1/\lambda$ 4420 and 4890 correspond to the two characteristic bands of biphenylen oxide, and those at 3220 and 3300 are the characteristic bands of the bromine atoms introduced. These latter two bands are to be attributed to the presence of bromine at the positions 6 and 2 respectively. Therefore, so far as it goes at least, the additivity of the characteristic absorption bands may be detected in this case.

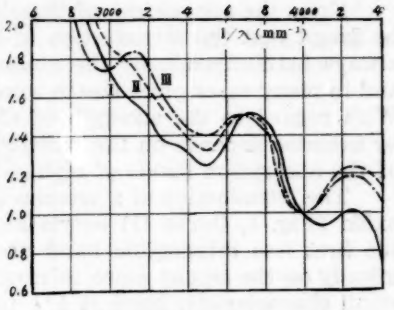
As will be seen from the curves in Figs. 3 and 4, however, the characteristic bands of the bromine atoms in a polybromobiphenylene oxide are not always developed separately, but rather partly or perfectly overlap one another in many cases, the curve of the polybromo-compound being often simpler than those of the lower bromo-compounds. In the 2,3,6-tribromo- and 2,3,6,7-tetrabromo-compounds (Fig. 3, Curve II and Fig. 4, Curve II), for example, though the characteristic band of the bromine atom at the position 2 or 7 can be found, the same at 3 and 6 can not be perceived in their curves, and in the 1,3,6,7-tetrabromo-compound (Fig. 4, Curve III) even none of them comes out in its curve. 1,3,6,8-Tetrabromobiphenylene oxide, however, gives a special curve (Fig. 4, Curve IV), and it possesses two characteristic bands at $1/\lambda$ 3100 and 3220 besides those at 3400 and 3780 which characterize the parent compound. As the band at 3220 of the former two corresponds to the characteristic band of the bromine atom at the position 3 or 6, the band at 3100 must be attributed to the same atom at 1 or 8.

A support for this view may be found in the comparisons between the absorption spectra of 1,3,6-trinitro- and 8-bromo-1,3,6-trinitro-biphenylene oxides (Fig. 5, Curves I and II) on the one hand and also among those of 1,6-dinitro-, 3-bromo-1,6-dinitro- and 3,8-dibromo-1,6-dinitro-bipheny-



I 1,3,6-Trinitro-biphenylene oxide.
II 8-Bromo-1,3,6-trinitro- ,, ,, .

Fig. 5. M/10000 alcoholic solutions.



I 1,6-Dinitro-biphenylene oxide.
II 3-Bromo-1,6-dinitro- ,, ,, .
III 3,8-Dibromo-1,6-dinitro- ,, ,, .

Fig. 6. M/10000 alcoholic solutions.

lene oxides (Fig. 6, Curves I, II, and III) on the other hand, because the compounds alone that have bromine at the position 8 give a distinct selective absorption band respectively in the neighbourhood of $1/\lambda$ 3000.

Experimental.

(1) *1,3,6- and 2,3,6-Trinitrobiphenylene oxides from 3,6-Dinitrobiphenylene oxide.* 3,6-Dinitrobiphenylene oxide (5.16 g.) was dissolved in fuming nitric acid (d 1.52; 20 c.c.) at room temperature and after being kept for 10 minutes at this temperature the reaction mixture was poured into water, when the reaction product separated as yellow precipitates. The trinitrobiphenylene oxides thus obtained (Yield almost theoretical) were extracted with a mixture of acetone and alcohol, and the residue was recrystallized from a small quantity of acetone, colourless rectangular plates melting at 311–312° (corr.) (Yield 0.28 g., 4.6% of the theoretical. Found: N, 13.92. Calc. for $C_{12}H_7O(NO_2)_3$: N, 13.87%). The acetone-alcoholic extract was evaporated and the crystals separated on cooling were recrystallized from acetic acid, colourless needles melting at 236–237° (corr.) (Yield 3.61 g., 60% of the theoretical. Found: N,12.82. Calc. for $C_{12}H_7O(NO_2)_3$: N, 13.87%). No depression of the melting point was observed each time when the former trinitro-compound was mixed with 1,3,6-trinitrobiphenylene oxide[4] obtained from 1,6-dinitrobiphenylene oxide, and the latter one, with 2,3,6-trinitrobiphenylene oxide[5] obtained from 2,6-dinitrobiphenylene oxide.

(2) *1,3,6,7- and 2,3,6,7-Tetranitrobiphenylene oxides from 2,3,6-trinitrobiphenylene oxide.* 2,3,6-Trinitrobiphenylene oxide (3.01 g.) was heated for one hour with fuming nitric acid (d 1.52; 15 c.c.) on the water bath and the reaction mixture was poured into water, giving pale yellow precipitates. The reaction product was recrystallized from acetic acid, colourless rectangular plates melting at 285–286° (corr.) (Yield 1.83 g., 53% of the theoretical. Found: N, 16.23. Calc. for $C_{12}H_4O(NO_2)_4$: N, 16.10%). The mother-liquor was concentrated and then diluted with water precipitating the other component of the nitration product. The precipitates were extracted with much alcohol to remove the contaminated sparingly soluble component and the extract was evaporated to dryness and then recrystallized repeatedly from benzene, colourless needles melting at 249–250° (corr.) (Yield 0.35 g., 10% of the theoretical. Found: N, 15.98. Calc. for $C_{12}H_4O(NO_2)_4$: N, 16.10%). No depression was observed

(4) S. Yamashiro, *J. Chem. Soc. Japan*, **59** (1938), 449.
(5) S. Yamashiro, *ibid.*, **59** (1938), 450.

in the mixed melting points of these nitration products when the higher melting one was mixed with 2,3,6,7-tetranitrobiphenylene oxide obtained from 2,3,7-trinitrobiphenylene oxide, and the lower melting one, with 1,3,6,7-tetranitrobiphenylene oxide obtaind from 1,3,6-trinitrobiphenylene oxide.

(3) *3-Bomo- and 3,6-dibromobiphenylene oxides from biphenylene oxide.* In the hope of obtaining the theoretical quantity of dibromobiphenylene oxides, biphenylene oxide (84 g.) was heated for 60 hours with bromine (160 g.) in boiling carbon tetrachloride (500 c.c.), but the bromination was incomplete. After the remaining bromine and the solvent had been distilled off, the reaction product (144.6 g.) was washed with hot water and recrystallized from acetic acid, colourless rectangular plates, m.p. 199–200° (corr.) (Yield 41 g. Found: Br, 49.12. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). The more soluble part was recovered from the mother-liquor and extracted with much hot alcohol to remove the sparingly soluble (in alcohol) dibromo-compound. The monobromo-compound was obtained on concentrating the alcoholic extract and recrystallized from the same solvent, colourless plates, m.p. 109–110° (corr.) (Yield 15 g. Found: Br, 32.31. Calc. for $C_{12}H_7OBr$: Br, 32.36%). Judging from the literature on the bromo derivatives of biphenylene oxide, this monobromo-compound must be 3-bromobiphenylene oxide and the dibromo-compound obtained above, 3,6-dibromobiphenylene oxide. The alcoholic mother-liquor was evaporated to dryness and the residue was extracted with cold ligroin, 3-bromobiphenylene oxide being almost removed. The ligroin extract was again evaporated to dryness and the residue was recrystallized from alcohol in the hope of isolating 2-bromobiphenylene oxide, but in vain.

(4) *2,6- and 2,7-Dibromobiphenylene oxides from 2-bromobiphenylene oxide.* 2-Bromobiphenylene oxide was prepared from 2-aminobiphenylene oxide by means of the Sandmeyer's diazo-reaction described by E. Noelting and his co-workers[6] and purified by sublimation and recrystallization from alcohol, colourless hexagonal plates, m.p. 121–122° (corr.) (Yield 56%). 2-Hydroxybiphenylene oxide described by K. Tatematsu and B. Kubota[7], m.p. 139–139.5° (corr.), was also obtained as a by-product, yield 5%.

2-Bromobiphenylene oxdie (15 g.) was heated for 48 hours with bromine (10 g.) in boiling carbon tetrachloride (50 c.c.) and after addition of acetic acid (50 c.c.), heating was continued until the colour of bromine disappeared. When the solvents were almost recovered by distilation from the reaction mixture, the residue was diluted with water. The reaction product thus separated (Yield 21.5 g.) was repeatedly extracted with hot alcohol and the residue was recrystallized from a small quantity of acetone, colourless needles, m.p. 178–179° (corr.) (Yield 9.2 g., 46.5%. Found: Br, 49.20. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). The crystals separated on cooling from the alcoholic extracts were repeatedly recrystalliezd from a mixture of acetone and alcohol, colourless needles, m.p. 199–200° (corr.) (Yield 0.4 g., 2.2%. Found: Br, 49.15. Calc. for $C_{12}H_6OBr_2$: Br, 49.03%). It was found very difficult to gather more crop of the last crystals, owing to the resemblance between the solubilities of those isomers. Judging from the literature on the dibromobiphenylene oxides (2,3-dibromo compound, m.p. 150–150.5°[1] and 2,6-dibromo compound, m.p. 176°[2] and also from the orientation of bromine which has been mentioned in the introductory part of this paper, the lower melting isomer of those reaction products must be 2,6-dibromobiphenylene oxide, and the higher melting one, 2,7-dibrobiphenylene oxide.

(5) *2,3,6-Tribromo- and 2,3,6,7-tetrabromo-biphenylene oxides from 3,6-dibromobiphenylene oxide.* 3,6-Dibromobiphenylene oxide (16.3 g.) was heated for 12 hours with a large excess of bromine (30 g.) in boiling acetic acid (500 c.c.), when the colour of bromine disappeared. The reaction mixture was concentrated, diluted with water, and the reaction product thus separated was filtered and dried (Yield 22 g.). After extraction with carbon tetrachloride, the sparingly soluble part of the reaction product was recrystallized fom toluene, large colourless needles, m.p. 306–307° (corr.) (Yield 4 g. Found: Br, 66.15. Calc. for $C_{12}H_4OBr_4$: Br, 66.05%). The carbon tetrachloride extract was evaporated to dryness, the residue was fractionally extracted

(6) E. Noelting, A. Braun and G. Thesmar, *Ber.* **34** (1901), 2253.
(7) K. Tatematsu and B. Kubota, this Bulletin, **9** (1934), 452.

with acetone, and the fraction melting at 193–198° (uncorr.) was recrystallized from acetone, colourless needles, m.p. 202–203° (corr.) (Yield 8.6 g. Found: Br, 59.34. Calc. for $C_{12}H_5OBr_3$: Br, 59.20%). Both of those bromination products gave no depression of their melting points when the tribromo compound was mixed with the corresponding compound obtained from 2,6-dibromobiphenylene oxide, and the tetrabromo-compound, with the corresponding compound obtained from 2,7-dibromobiphenylene oxide. Those products, therefore, were evidently identified respectively as 2,3,6-tribromobiphenylene oxide and 2,3,6,7-tetrabromobiphenylene oxide.

(6) *2,3,6,7-Tetrabromobiphenylene oxide from 2,7-dibromobiphenylene oxide.* 2,7-Dibromobiphenylene oxide (0.2 g.) was heated for 4 hours with a large excess of bromine (2 g.) in boiling glacial acetic acid (40 c.c.), when the colour of bromine disappeared. The crystals separated on cooling from the reaction mixture were recrystallized from toluene, colourless needles, m.p. 306–307° (corr.) (Yield 0.21 g., 71%). The good yield of this 2,3,6,7-tetrabromo-compound from 2,7-dibromobiphenylene oxide owes to the fact that the most favourable positions 3 and 6 for the introduction of bromine remains free in the last compound.

(7) *2,3,6-Tribromo- and 1,3,6,7- and 2,3,6,7-tetrabromo-biphenylene oxides from 2,6-dibromobiphenylene oxide.* 2,6-Dibromobiphenylene oxide (3.26 g.) was heated for 12 hours with bromine (6 g.) in boiling glacial acetic acid (100 c.c.), when the colour of bromine disappeared. After distillation of the solvent, the reaction mixture was diluted with water to the precipitation of a white crystalline mass, which was filtered, dried (Yield 4.4 g.) and then extracted with hot benzene. From the sparingly soluble residue, 2,3,6,7-tetrabromobiphenylene oxide was isolated by recrystallization from toluene in large colourless needles, m.p. 306–307° (corr.) (Yield 1.6 g.). The benzene extract was evaporated to dryness and fractionated into 10 parts by means of the fractional extraction of the residue with acetone. Of these fractions the part melting at 238–240° (uncorr.) was recrystallized from toluene, colourless needles, m.p. 248–249° (corr.) (Yield 0.3 g. Found: Br, 66.08. Calc. for $C_{12}H_4OBr_4$: Br, 66.05%) and the part melting at 196–198° (uncorr.) was recrystallized from acetone to the isolation of 2,3,6-tribromobiphenylene oxide, colourless needles, m.p. 202–203° (corr.) (Yield 0.8 g.). The lower melting tetrabromo-compound obtained here was identical with the corresponding compound which was obtained as a by-product from 2,3,6-tribromobiphenylene oxide and consequently concluded to be 1,3,6,7-tetrabromobiphenylene oxide.

(8) *1,3,6,7- and 2,3,6,7-Tetrabromobiphenylene oxides from 2,3,6-tribromobiphenylene oxide.* 2,3,6-Tribromobiphenylene oxide (1 g.) was heated for 12 hours with a large excess of bromine in boiling acetic acid (200 c.c.), the solvent was distilled off and the residue was then diluted with water. The reaction product thus separated was filtered, dried, and after extraction with benzene, recrystallized from toluene, colourless needles of 2,3,6,7-tetrabromobiphenylene oxide, m.p. 306–307° (corr.) (Yield 0.6 g.). The benzene extract was evaporated to dryness, the residue was repeatedly extracted with ligroin, and the sparingly soluble part was recrystallized from toluene, colourless needles of 1,3,6,7-tetrabromobiphenylene oxide, m.p. 248–249° (corr.) (Yield 0.06 g.). 2,3,6-Tribromobiphenylene oxide was recovered from the ligroin extract.

(9) *1,3,6,8-Tetrabromobiphenylene oxide from 3,6-dibromo-1,8-dinitrobiphenylene oxide.* (i) 1,8-Diamino-3,6-dibromobiphenylene oxide. 3,6-Dibromo-1,8-dinitrobiphenylene oxide (2.08 g.) was heated with stannous chloride (10 g.) and concentrated hydrochloric acid (10 c.c.) in boiling acetone (300 c.c.), when the colourless needle crystals of 1,8-diamino-3,6-dibromobiphenylene oxide dihydrochloride separated; which were filtered on cooling and washed successively with hydrochloric acid, water and then with acetone. The filtrate was distilled to the recovery of acetone, dilute hydrochloric acid was added and the second crop of the dihydrochloride thus separated was treated as before (Yield 2.07 g., 97%). The dihydrochloride was converted into the free base by treating it with an excess of sodium acetate solution, and was recrystallized from chloroform, small colourless needles which take blue colour on standing in the wet air, m.p. 276.5–277.5° (corr.) (Found: N, 7.94. Calc. for $C_{12}H_4OBr_2(NH_2)_2$: N, 7.87%). 1,8-Diamino-3,6-dibromobiphenylene oxide is soluble easily in acetone and ethyl acetate, moderately in benzene and chloroform, but difficultly in alcohol, ether, ligroin, and carbon tetrachloride. The dihydrobromide of this base was obtained by

treating the base with hydrobromic acid in acetone solution, colourless needles (Found: Br, 61.58. Calc. for $C_{12}H_4OBr_2(NH_2)_2$ 2HBr: Br, 61.77%).

(ii) 1,8-Biacetamino-3,6-dibromobiphenylene oxide, 1,8-Diamino-3,6-dibromobiphenylene oxide (0.178 g.) was heated with a mixture of glacial acetic acid (2 g.) and acetic anhydride (0.1 g.), and diluted with water, when a white crystalline mass separated. The reaction product (Yield 0.222 g.) was recrystallized from alcohol, small colourless needles, m.p. 358–360° (corr.) (Found: N, 6.42. Calc. for $C_{12}H_4OBr_2(NHCOCH_3)_2$: N, 6.36%). It is soluble fairly in acetone, alcohol, and acetic acid, but sparingly in the other ordinary organic solvents.

(iii) 1,3,6,8-Tetrabromobiphenylene oxide. Finely powdered 1,8-diamino-3,6-dibromobiphenylene oxide (1.39 g.) was suspended in 10% hydrobromic acid, and was diazotized with sodium nitrite (0.46 g.) under ice cooling, when the base changed slowly into the yellow diazo-compound. Cuprous bromide, on the other hand, was prepared by heating a mixture of crystalline copper sulphate (1.8 g.), copper bronze (0.7 g.), potassium bromide (3 g.), concentrated sulphuric acid (0.8 g.) and water (12 c.c.) until the blue colour of the cupric salt disappeared. After being washed with cold air-free water, cuprous bromide was added to the above-mentioned ice-cold suspension of the diazo-compound. This mixture was allowed to stand overnight under cooling and then gradually heated on the water bath to complete the decomposition of the diazo-compound, when the brown solid separated out. The reaction product was filtered, washed well with hot water, dried and extracted with benzene. The extracted was evaporated to dryness and, after being extracted again with acetone to the removal of the easily soluble impurity, the residue was recrystallized from carbon tetrachloride, pale yellow small needles, m.p. 237–238° (corr.) (Yield 0.51 g. Found: Br, 65.01 Calc. for $C_{12}H_4OBr_4$: Br, 65.05%).

Summary.

For the purpose of confirming the constitution of the polybromo-compounds obtained directly from biphenylene oxide by bromination, the following experiments were performed by the present author:

(1) Verification of the formation of 2,3,6-trinitro- and 1,3,6,7- and 2,3,6,7-tetranitro-biphenylene oxides from 3,6-dinitrobiphenylene oxide and of the formation of 2,3,6-tribromo- and 1,3,6,7- and 2,3,6,7-tetra-bromo-biphenylene oxides from 3,6-dibromobiphenylen oxide.

(2) Isolation of 2,7-dibromobiphenylene oxide from the bromination products of 2-bromobiphenylene oxide, and preparation of 1,3,6,8,-tetra-bromobiphenylene oxide from 3,6-dibromo-1,8-dinitrobiphenylene oxide.

(3) Comparative studies on the characteristics and the absorption spectra of biphenylene oxide and its bromoderivatives.

In conclusion, the author wishes to express his hearty thanks to Prof. R. Majima of the Osaka Imperial University and Shigemi Ôba, the principal of the Yonezawa Higher Technical School, for their kind advices and encouragements. A part of the expense of this investigation has been defrayed from the grant of the Nippon Gakuzyutu Sinko-kwai (the Japan Society for the Promotion of Scientific Research) for which also the author wishes to record his thanks.

Yonezawa Higher Technical School.

Polymerisation of Tung Oil, IV. Effects of Various Natural Fatty Oils upon the Gelation of Tung Oil.

By Monzi TATIMORI.

(Received November 28, 1940.)

It is well known that the gelation of tung oil on heating may be delayed or prevented by the addition of certain substances. Considerable amount of works have been done along this line,[1] but as to the quantitative relation between gelation time and the amount of substances added to tung oil, only a few informations have been published.

There are known various types for curves of the gelation time and the amount of added substances, but as for the nature of the curve nothing is said. The work described in this article was undertaken for the purpose of determining the comparative effects of various fatty oils in preventing the gelation of tung oil on heating, with a hope to throw light on the explanation of gelation phenomenon of tung oil.

Experimentals. The apparatus consists of an oil bath (the diameter being 20 cm., height 17 cm.) which was maintained at a required constant temperature. The cover of the bath is provided with four openings through which the ordinary test tube, whose size was predetermined by measuring the height of 5 c.c. of alcohol taken in it (expressed in cm. unit), was dipped in bath so that the lower 9 cm. of the test tube was immersed in the oil. Five c.c. of a mixture, containing known proportion of tung oil and added substances, was put in a test tube, a glass rod (its diameter being 3 mm., length 16 cm.) was inserted in, and the test tube was put into the oil bath. The time required for the oil to gelatinize was then measured and noted. The determination was repeated for the same mixture a few times and the mean value was calculated.

The samples used have the following constants (Table 1).

Table 1.

Kind of oils	d_{15}^{15}	n_D^{20}	Iodine value	Acid value
Tung oil (A)	0.942	1.518	164.5	3.17
Tung oil (C)	0.941	1.517	166.8	4.64
Japanese wood oil	0.935	1.501	168.2	1.44
Perilla oil	0.935	1.483	199.3	5.71

(1) R. Bürstinbinder, *Farben Ztg.*, **23** (1917), 243; *Chem. Umschau Fette, Oele Wachse*, **36** (1929), 36; Krumbhaar, *Chem. Abstrs.*, **9** (1915), 2155; J. Marcusson, *Zt. deut. Oele Fette Ind.*, **43** (1923), 162; H. Hardert, *Farbe und Lack*, 1928, 558; H. Brendel, *ibid.*, 1932, 145; L. A. Jordan, *J. Oil Colour Chem. Assoc.*, **17** (1934), 47.

Table 1.—(*Concluded*)

Kind of oils	d_{15}^{15}	n_D^{20}	Iodine value	Acid value
Linseed oil	0.934	1.480	171.1	4.31
Hemp seed oil	0.927	1.479	162.7	2.08
Soya bean oil	0.922	1.475	131.4	1.12
Maize oil	0.923	1 475	122 1	0 94
Sesame oil	0.923	1.474	115.2	1.19
Rape oil	0.917	1 473	99 4	1.90
Olive o l	0.918	1.470	83.0	4 37
Camellia oil	0.917	1.469	80 9	3.43
Castor oil	0.975	1.479	84.8	1.79
Sardine oil	0.934	1.483	194.4	4 66
Hardened fish oil	—	—	17.1	2.24
Liquid paraffin	0.882	1.479	—	—

From the preliminary experiments it was found that the gelation time is affected by the heating temperature, by the size of the test tube as well as by the kind of tung oils.

One of the examples is shown in Table 2, in which the gelation time of tung oil (A) were measured at 290°C. in three kinds of test tubes, widely different in size.

Table 2.

% of linseed oil added to tung oil	Gelation time in sec. Size of test tube (he ght of 5 c.c. in cm.)		
	3.1 cm.	3.5 cm.	4.5 cm.
0	485	478	465
10.00	565	559	549
15.01	633	623	620
20 04	701	699	685

The absolute value of the gelation time is affected remarkably by the size of test tube. The relation between the reciprocals of the gelation time (t) and percentage of linseed oil (x) are shown in Fig. 1.

It is a very important new fact that in all cases $1/t$ and x are in linear relations and the limiting value of x at $t=\infty$ (hereafter denoted as x_∞) converge on one point, in spite of wide differences in dimension of test tubes.

(1) *Gelation time for the system of Japanese wood oil and tung oil (A).*

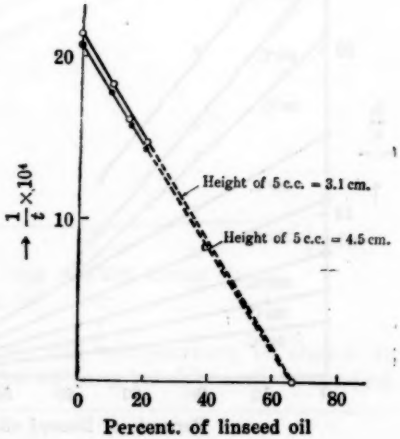


Fig. 1.

Results at 290°C. in test tubes of 3.7 cm. are given in Table 3.

Table 3.

Percent. of Japanese wood oil added to tung oil.	Gelation time (sec.)
0	467
10	513
20	555
30	640
40	730
50	862
60	1033
70	1237
100	3848

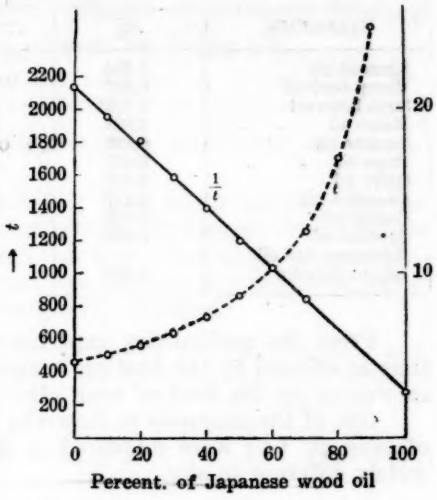


Fig. 2.

The relations of $t-x$ and $1/t-x$ are shown in Fig. 2. x and $1/t$ form a straight line in the whole range of Japanese wood oil.

(2) *The gelation time of the system of tung oil and linseed oil.* From the preliminary experiments it was noticed that the amount of added substance necessary to make the gelation time of tung oil be infinitely long, increases a little, when the heating temperature falls from 290 to 280°C., so the gelation time of the system of tung oil and linseed oil was measured in wide temperature range. It was found that the temperature of 270°C. is most suitable to determine the relation between $1/t$ and x.

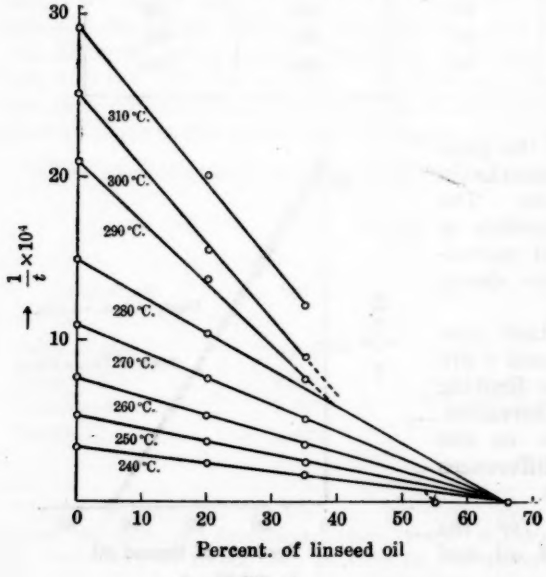


Fig. 3.

The results are shown graphically in Fig. 3.

From Fig. 3 it was found that below 280°C. lines of $1/t$- x converge

on one point of 67% and above 290°C. they shift gradually to the origin according as temperature increases: above 310°C. the rectilinear relationship is no more formed. The temperature of 270°C. is the most suitable for measuring the time of gelation by reason that above this temperature relation of $1/t-x$ is unstable and below this temperature the gelation time becomes too great.

The values of x at $\frac{1}{t}=0$ (x_∞) obtained from graphs are shown in Table 4.

Table 4.

Temperature (°C.)	x_∞ (%.)
305	52.0
300	54.0
295	56.5
290	61.5
280	67.0
270	67.0
260	67.0
250	66.5
240	67.5

(3) *Effects of temperature upon the gelation time.* The gelation time of tung oil is prolonged by lowering the heating temperature. L. A. Jordan and W. E. Wornum[2] measured the gelation time of many kinds of tung oils. F. T. Walker[3] treated their results and stated that the relation of the gelation time and temperature can be expressed by a hyperbola, whose equation is $(T-m)\times t=k$, where m and k denote constants, T the temperature, t the gelation time.

If the above be true, $1/t$ and T should be in linear relation. From Fig. 4. neither from the case of tung oil only, nor from that added by 20% linseed oil straight lines can be obtained.

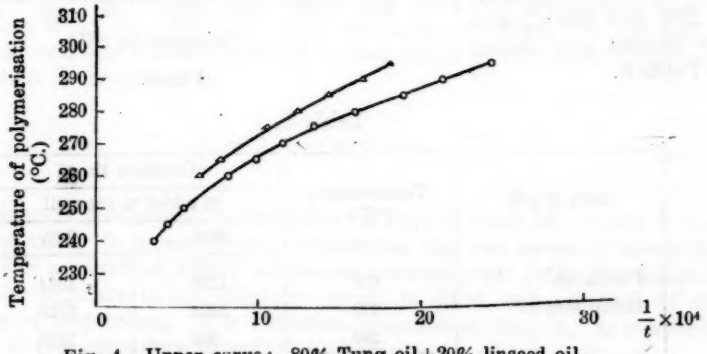


Fig. 4. Upper curve: 80% Tung oil+20% linseed oil.
Lower curve: Tung oil.

The relation between gelation time and temperature is shown in Fig. 5. It is seen that the gelation time of tung oil decreases according

(2) *J. Soc. Chem. Ind.*, **53** (1934), 1.
(3) *Ibid.*, **53** (1934), 104.

to increasing degree of temperature, but at temperature higher than 300°C. the decreasing amounts become less and less, and at last the gelation time of the system containing 20% linseed oil reaches a minimum value at 330°C., then again it increases.

It is known that the acidic substance prevents the gelation and also that when the fatty oil is heated at high temperature the cracking of glycerine radical occurs,[4] so it is reasonable that at high temperature the gelation of tung oil is prolonged.

(4) *Effects of various fatty oils.* The gelation time of various fatty oils mixed in tung oil (C) was measured at 270 and 280°C. and the results are shown in Table 5.

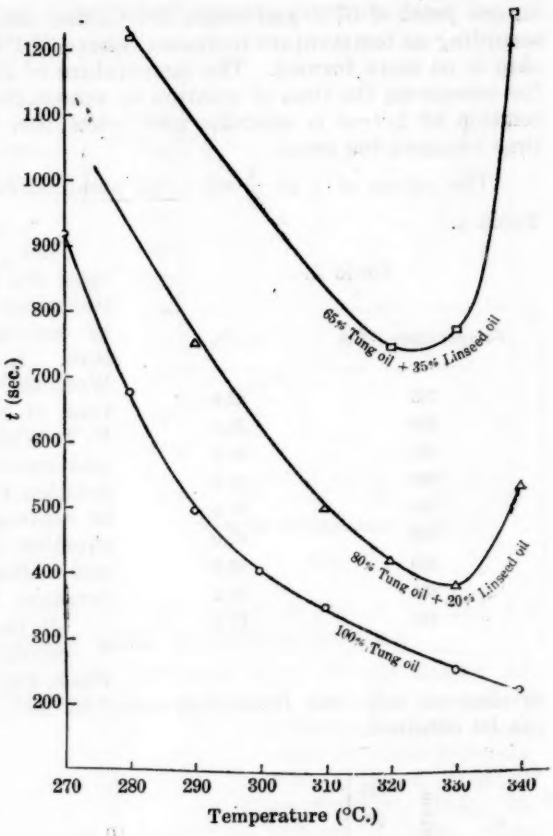


Fig. 5.

Table 5.

Kind of oils	Temperature (°C.)	Gelation time	
		% added to tung oil	
		20%	30%
Perilla oil	270	1298	1534
Hemp seed oil	270	1324	1710
	280	952	1216
Soya bean oil	270	1325	1727
	280	1023	1309
Maize oil	270	1353	1742
	280	1001	1293

(4) R. Sändig, Dissertation, Leipzig (1934), 26; Kürz, *Zt. angew. Chem.*, **49** (1936), 235.

Table 5.—(*Concluded*)

Kind of oils	Temperature (°C.)	Gelation time	
		% added to tung oil	
		20%	30%
Rape oil	270	1396	1823
	280	989	1364
Camellia oil	270	1434	1879
	280	1044	1408
Sesame oil	270	1485	2079
	280	1120	1638
Castor oil	270	1393	1815
Sardine oil	270	1483	1983
	280	1075	1440
Hardened fish oil	270	1351	1745
	280	957	1213
Liquid paraffin	270	1397	1873
	280	982	1355

For any oil $1/t$ and x are in linear relation and the lines of 270 and 280°C. converge on one point.

Discussion of Results. The gelation time of tung oil within the limit of experiments is prolonged by the addition of other fatty oil without exception. The retarding nature of any fatty oils are similar to that of Japanese wood oil (Fig. 2). For any kind of added oils $1/t$ and x show linear relation when measured in test tubes of the same dimension. This relation is expressed by

$$\frac{1}{t} = \frac{1}{t_0} - ax = b - ax \,, \qquad (1)$$

where a denotes a constant, t_0 the gelation time of tung oil. a and b vary widely according to experimental conditions, but the value of x when $t = \infty$, i.e. the amount of added substance necessary to make the gelation time of the mixture to be infinitely great, is fixed, not affected by the dimension of test tubes. It is therefore considered that x_∞ is a specific property of the substance in gelation phenomenon of tung oil.

x_∞ of various oils at 270 and 280°C. are shown in Table 6.

From the above table it is concluded that drying oils such as perilla, linseed, hempseed are less effective and for the perfect prevention of gelation the amount of more than 67% of them should be added, while semi- and non-drying oils are more effective. This is expected from the fact that at high temperature the drying oils have themselves the tendency of polymerisation and gel-formation.

Table 6—x_∞ (%).

Kind of oils	270°C.	280°C.
Perilla oil	75.5	—
Linseed oil	67.0	67.0
Hemp seed oil	67.0	69.0
Maize oil	64.5	64.5
Soya bean oil	63.0	63.5
Rape oil	63.0	63.5
Camellia oil	59.0	59.0
Sesame oil	53.0	54.5
Sardine oil	58.0	59.0
Hardened fish oil	65.0	66.5
Castor oil	62.0	—
Liquid paraffin	60.4	60.7

As a general idea x_∞ of common fatty oils increases according to increase of iodine values. The effects of castor oil, hardened fish oil and liquid paraffin were measured for the purpose of comparison, they have specific effects respectively.

Summary.

(1) The gelation time of the system of tung oil and linseed oil was measured at 240–310°C. In the range of 240–280°C. the lines of $1/t$–x converge on one point.

(2) The relation between gelation time and the amount of addition of any fatty oil is expressed by $1/t=1/t_0-ax$, and the value of x at $t=\infty$ is considered as a characteristic constant of added fatty oil.

(3) Gelation preventing effects of various natural fatty oils were measured at 270 and 280°C. Drying oils are less effective than non-drying oils due to their tendency of polymerisation.

(4) The temperature dependance of gelation time was discussed.

In conclusion, the author wishes to express his sincere thanks to Dr. K. Baba, Dr. T. Yosioka, and Mr. K. Yokota for their kind guidance.

Laboratory of Hitachi Works,
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The Nature of the Complex Formation between Boric Acid and Organic Polyoxy Compounds.

By Yojiro TSUZUKI.

(Received December 21st, 1940.)

It is a well-known fact that complex compounds are formed between boric acid and polyoxy compounds. The compositions have been estimated by means of various methods, and even definite compounds have been isolated.[1] It has not been elucidated, however, under what conditions the complexes are formed. The author has previously shown that free boric acid forms complexes only in little quantity with diols such as ethyl tartrate, while alkali borates combine with it to a large extent.[2] Thus the author has stated that only borate ion combines with diols, but free boric acid does not, since it gives in aqueous solution only a small quantity of BO_2', and it has been suggested that complexes (similar to boric acid complex) can be formed in general between polyoxy compounds, only when one reactant is in ionic state.

The present work deals with the polarimetric studies on the complex formation between boric acid and polyoxy compounds of various types (mannitol, glucose, tartaric acid, tartrates, gluconate) carried out in order to elucidate the nature of the complex formation.

The experimental results will be described and discussed with each polyoxy organic compound.

Mannitol. It is known that mannitol shows a very feeble laevorotation, which is scarcely changed by the addition of free boric acid,[3] but in the presence of alkali borate, the solution shows strong dextrorotation.[4] It was shown several years ago by Böeseken and Vermaas[5] that, in the solutions of mannitol in water with $NaBO_2$, there exist complex ions of the formula BD' and BD_2', where D represents a molecule of a polyhydric alcohol. The author has now observed the variation in the optical rotation of mannitol with the change of BO_2' concentration in the mannitol-boric acid system. The results are shown in Fig. 1 and described in Table 1.

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(1) Lowry, *J. Chem. Soc.*, **1929**, 2853; Bancroft and Davis, *J. Phys. Chem.*, **34** (1930), 2479; Lowry, "Optical Rotatory Power," 290, London (1935).

(2) Y. Tsuzuki, this Bulletin, **13** (1938), 337 (by distribution method); Y. Tsuzuki and Y. Kimura, this Bulletin, **15** (1940), 27 (by polarimetric method).

(3) J. M. Braham, *J. Am. Chem. Soc.*, **41** (1919), 1707; F. B. Marti, *Bull. Soc. chim. Belg.*, **39** (1930), 590.

(4) Vignon, *Compt. rend.*, **77** (1873), 1191; *Ann. chim. phys.*, [5], **2** (1874), 440; E. Fischer, *Ber.*, **23** (1890), 385.

(5) J. Böeseken and N. Vermaas, *Rec. trav. chim.*, **54** (1935), 853.

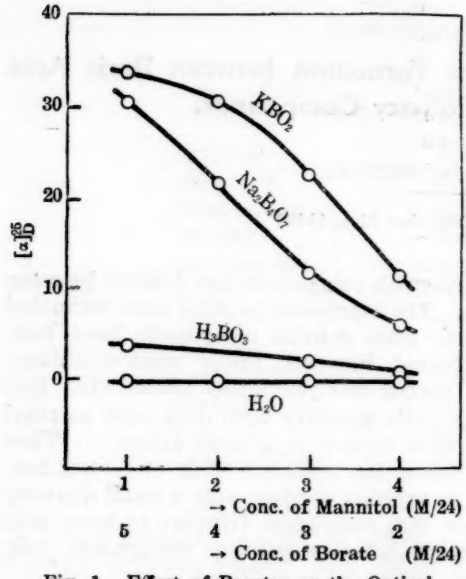
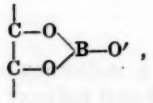


Fig. 1. Effect of Borates on the Optical Rotation of Mannitol.

The experiments indicate that complex formation proceeds with the increase of the concentration of borate ion. Borate ion enhances the rotation of mannitol because it gives a complex with the cyclic



structure, which is assumed to have a large optical rotation, since the free rotation of the OH groups in the molecule is inhibited. The quantity of this complex compound will be increased if the concentration of BO_2' becomes greater, inasmuch as equilibrium exists between these substances.

$$\underset{\text{feeble rotation}}{C_6H_{12}O_6} + BO_2' \rightleftarrows \underset{\text{strong rotation}}{\text{Mannito-borate}} + H_2O\,.$$

It is, therefore, due to the greater concentration of BO_2' that KBO_2 has a stronger effect than borax of the same molar concentration with respect to B-atom.

Mention should be made here to the well-known fact that boric acid can be titrated with alkali in the presence of mannitol (as well as glycerol), although it is in itself a very weak acid. It appears, therefore, that free boric acid can form complex compounds of a strongly acidic character with these polyhydric alcohols, but this fact is to be explained in the following way. In the titration of boric acid in the presence of mannitol, mannito-boric acid is formed from mannitol and borate ion. This complex which has a strongly acidic character can be formed in a measurable quantity, only after adding a certain amount of alkali, and the quantity of this complex is gradually increased with the progress of titration, thus in the presence of excess mannitol, all the boric acid can be titrated, since it can then be totally converted into strongly acidic complex acid.

Glucose. Darmois and Peyroux[6] have shown that H_3BO_3 even at saturation is without effect on the rotation of glucose, but that sodium borates have a large effect. Murgier and Darmois[7] came to the con-

(6) Darmois and Peyroux, *Compt. rend.*, **193** (1931), 1182.
(7) Murgier and Darmois, *Angew. Chem.*, **51** (1938), 753, X International Congress for Chemistry in Rome, May 1938.

clusion by examining optical rotation that H_3BO_3 gives with hexoses a very small amount of complexes, while $NaBO_2$ gives a well characterized compound.

The author has examined the effects of boric acid and its alkali salts on the rotation of glucose by varying the ratio Borate/Glucose (Fig. 2 and Table 2) as in the case of mannitol.

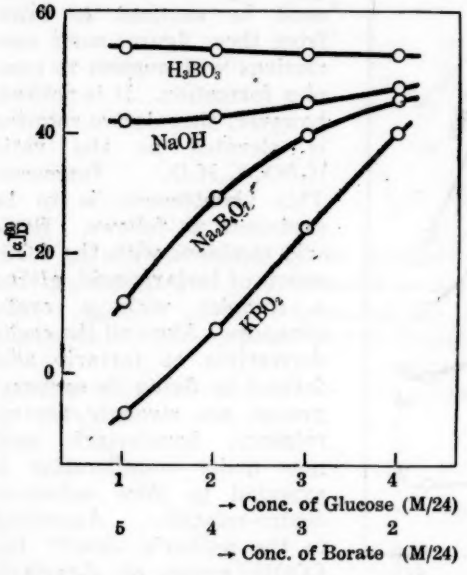


Fig. 2. Effect of Borates on the Optical Rotation of Glucose.

The experiment is in harmony with the statement of Darmois and his collaborators[8]. The specific rotation of glucose, whose large value is due to the cyclic structure of glucoside formula, suffers great changes in the presence of alkali borates, and indeed even negative rotation appears with the increase of the concentration of alkali borate. It is not improbable that the cyclic structure of glucose suffers some modifications by the alkalinity of borate salts, thus the strong dextro-rotation being depressed, but the actual effect of weak alkali on the rotation of glucose is very small (Table 2) and even stronger alkali such as NaOH does not exercise a remarkable influence (Fig. 2). We should, therefore, assign the radical change of the rotation to the complex formation between borate ion and glucose. The cyclic nature of the complex is responsible to the depression of the specific rotation of glucose. The general behaviours of glucose with respect to the change of optical rotation are very similar to that of mannitol, although it is in the opposite direction. This is, no doubt, due to the lack of carboxyl group.

Tartaric Acid and Alkali Tartrates. In these cases free boric acid has remarkable influence, in contrast to polyhydric alcohols. The complex formation between boric acid and tartaric acid and alkali tartrates, is due to the union of COO′ and $B(OH)_3$. Here the latter does not act as an ion, but as an undissociated polyoxy compound.

The reaction of these complex formations has been already examined, thus Darmois[9] has concluded from his polarimetric measurements that

(8) The author could not confirm the observation of P. S. Tang and P. N. Sung with regard to the effect of boric acid on glucose that the rotation of glucose shows the minimum value of $[\alpha]_D = +47°$ in the region of 0.2 M H_3BO_3. *Nature*, **137** (1936), 275.

(9) Darmois, *J. Chim. phys.*, **23** (1926), 649.

a complex $B(OH)_3 2C_4H_6O_6$ exists in the mixture of tartaric-boric acid. On the other hand he observed that in strong alkaline solution boric acid gives a laevo-rotatory complex salt.

The present author's observations on the effects of boric acid and borates on the rotation of tartaric acid are shown in Fig. 3 and Table 3. The results are apparently complicated, hence one must be cautious to draw from these figures some conclusions with respect to complex formation. It is noticed, however, that dextro-rotation is elevated as the ratio $H_3BO_3/C_4H_6O_6$ increases. This phenomenon is to be explained as follows. Boric acid combines with the COO′ group of tartaric acid, giving a complex with a cyclic structure. Since all the cyclic derivatives of tartaric acid formed by fixing its carboxyl groups are strongly dextro-rotatory, borotartaric acid now under consideration is expected to show enhanced dextro-rotation. According to the author's view[10] the COOH group of *d*-tartaric acid is a contributor of its laevo-partial rotation, and its characteristic (i.e. partial rotatory contribution) is enfeebled when it forms a cyclic structure, hence the dextro-partial rotation originating in the OH group predominates. Now the actions of borax on the rotation of tartaric acid (Table 3) are in fact similar to those of H_3BO_3 on sodium tartrate (Table 4). Of course this is due to the circumstances that in aqueous solution there takes place the following exchange reaction between these substances:

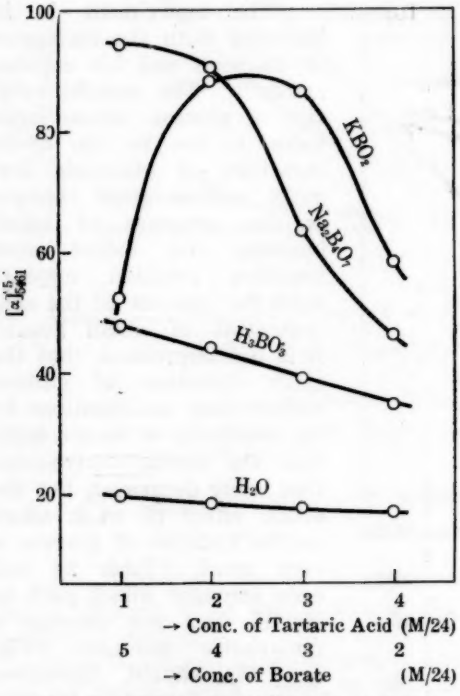


Fig. 3. Effect of Borates on the Optical Rotation of Tartaric Acid.

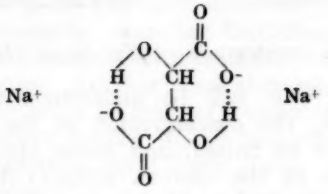
$$Na_2B_4O_7 + C_4H_6O_6 + 5H_2O = 4H_3BO_3 + C_4H_4O_2Na_2 .$$

Since these mixtures are always acidic, undissociable OH group is present in an appreciable quantity either in tartaric or in boric acid, and thus combination occurs between anion and OH group, leading to the formation of complexes, similar in structure to those of the free tartaric-boric acid system, but these complexes dissociate more strongly than the latter, so

(10) Y. Tsuzuki, *Sci. Pap. Inst. Phys. Chem. Res.*, **35** (1939), 425.

that the complex formation proceeds further, and thus strong dextro-rotation appears. With the increase of the ratio Borax/Tartrate, the concentration of alkali becomes greater. Hence the concentration of borate ion will be raised with the result that dextro-rotation is enhanced.

It is known that alkali tartrates show none of the optical anomalies of the acid[11] and exhibit considerably high specific rotation (Tables 4 and 5). This may be due to the formation of a somewhat fixed cyclic structure:



As already shown by the author[10] the (negative) partial rotation of the COOH group is enfeebled in a ring compound of this sort, and the (positive) partial rotation of the OH group becomes predominant; consequently the molecule shows strong dextro-rotation.

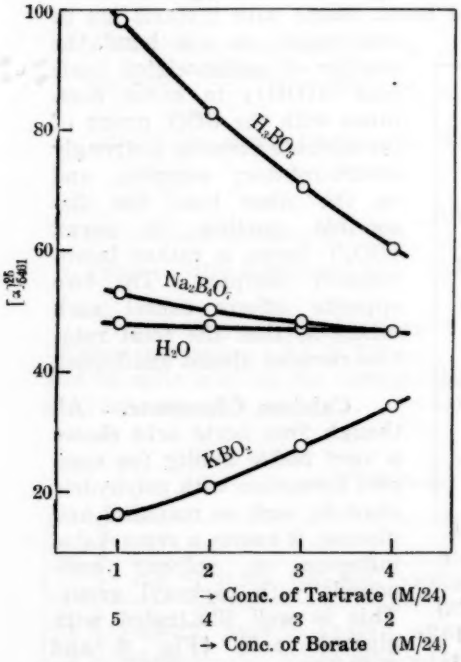


Fig. 4. Effect of Borates on the Optical Rotation of Sodium Tartrate.

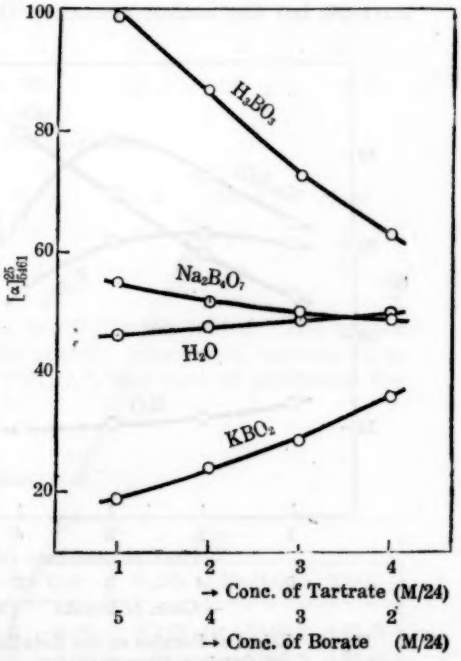


Fig. 5. Effect of Borates on the Optical Rotation of Potassium Tartrate.

(11) Lowry and Austin, Bakerian Lecture, *Phil. Trans.* A, **222** (1922), 249.

The action of KBO_2 on alkali tartrates depresses the high dextro-rotations of these salts, and indeed the effect becomes stronger as the concentration of BO_2' increases. (Fig. 4 and 5, Tables 4 and 5). This can be explained in the following way. Since BO_2' can not unite with the COO′ group of tartrates, it combines with their OH groups, the reaction being represented as follows:

$$BO_2' + \begin{matrix} HO-CH-COONa \\ | \\ HO-CH-COONa \end{matrix} \rightleftarrows O'B\begin{matrix} O-CH-COONa \\ | \\ O-CH-COONa \end{matrix} + H_2O\,.$$

Seeing that cyclic compounds of the type $R\begin{matrix} O-CH-COOR' \\ | \\ O-CH-COOR' \end{matrix}$ show strong laevo-rotation,[12] it will be understood that, with increasing concentration of KBO_2, the concentration of the complex with laevo-rotatory character will be raised, and hence the system becomes less dextro-rotatory. Thus in the system, $KBO_2 : C_4H_6O_6 = 20 : 10$ (Fig. 3, Table 3), which is equivalent to the system, $H_3BO_3 : C_4H_4O_6K_2 = 20 : 10$ (Fig. 5, Table 5) the specific rotation reaches the maximum value $[\alpha]_{5461}^{25} = +87.84°$ at this point, and by adding BO_2' further to this mixture, the high dextro-rotation of this system will be lowered.

Borax is nearly without effect on the rotation of alkali tartrates (Fig. 4 and 5, Tables 4 and 5). This phenomenon appears rather curious, but the author considers that borax reacts with tartaric ion in two ways: on one hand the portion of undissociated boric acid $B(OH)_3$ in borax combines with the COO′ group of the tartrate forming a strongly dextro-rotatory complex, and on the other hand the dissociable portion in borax (BO_2') forms a rather laevo-rotatory complex. The two opposite effects cancel each other, so that the total rotation remains almost unaffected.

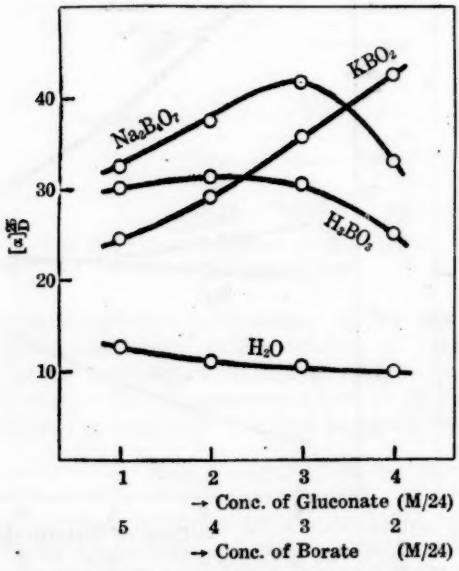


Fig. 6. Effect of Borates on the Rotation of Calcium Gluconate.

Calcium Gluconate. Although free boric acid shows a very feeble ability for complex formation with polyhydric alcohols, such as mannitol and glucose, it exerts a remarkable influence on polyoxy compounds with carboxyl group. This is well illustrated with gluconic acid (Fig. 6 and Table 6).

(12) Y. Tsuzuki, this Bulletin, **15** (1940), 27; *Sci. Pap. Inst. Phys. Chem. Res.*, **35** (1939), 425, 466; **36** (1939), 31.

As will be easily understood from the examples of tartrates, this phenomenon must be attributed to the presence of complexes formed between COO' and H_3BO_3. Calcium gluconate also shows somewhat complicated behaviours with alkali borates as in the cases of tartaric acid and its salts. It is remarkable that the dextro-rotation is lowered with the increase of KBO_2 concentration. This may, however, be explained as follows. In alkaline medium BO_2' unites no more with COO', but reacts with alcoholic hydroxyl groups, so that it is natural that the rotation suffers alteration in the other direction.

In conclusion it should be remarked that these reactions of complex formation arrive at equilibrium almost instantaneously. This is probably due to exchange reaction. In this connexion mention should be made further that heteropoly acids as well as isopoly acids in inorganic field are perhaps of the nature similar to the present cases, thus they may be explained from the point of view above stated.

Experimental Part.

Polarimetric measurements were made on the mixtures of the following compositions:

	No. 1	No. 2	No. 3	No. 4
M/4–Optically active compound c.c.	5	10	15	20
M/4-H_3BO_3, $\frac{Na_2B_4O_7}{4}$ or KBO_2 c.c.	25	20	15	10

Hence the concentrations in the mixtures are:

	No. 1	No. 2	No. 3	No. 4
Optically active compound M/24	1	2	3	4
Borate or other substances M/24	5	4	3	2

The numerical values are given in the following tables. The length of the observation tube is 2.2 dm. The specific rotation of tartaric acid and its salts is given for tartrate ion $C_4H_4O_6''$, and that of gluconate for gluconate ion $C_6H_{11}O_7'$.

Table 1. Mannitol.

No.	α				$[\alpha]_D^{25}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	−0.001	+0.06	+0.510	+0.564	−0.06	+3.59	+30.55	+33.78
2	−0.003		+0.722	+1.02	−0.09		+21.62	+30.54
3	−0.009	+0.09	+0.583	+1.13	−0.18	+1.80	+11.64	+22.56
4	−0.012	+0.05	+0.387	+0.746	−0.24	+0.60	+ 5.79	+11.17

Table 2. Glucose.

No.	α					$[\alpha]_D^{30}$				
	H_3BO_3	$Na_2B_4O_7$	KBO_2	K_2CO_3	NaOH	H_3BO_3	$Na_2B_4O_7$	KBO_2	K_2CO_3	NaOH
1	+0.888	+0.196	−0.107	+0.833	+0.696	+53.77	+11.87	− 6.48	+50.74	+42.14
2	+1.782	+0.979	+0.249	+1.683	+1.421	+53.94	+29.64	+ 7.54	+50.94	+43.02
3	+2.611	+1.97	+1.405	+2.528	+2.235	+52.70	+39.76	+24.36	+51.02	+45.10
4	+3.49	+3 002	+2.683	+3.385	+3.132	+52.83	+45.45	+40.25	+51.25	+47.41

Table 3. Tartaric Acid.

No.	α				$[\alpha]_{5461}^{25}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	+0.271	+0.652	+1.28	+0.711	+19.97	+48.03	+94.32	+52.38
2	+0.501	+1.20	+2.45	+2.385	+18.45	+44.19	+90.24	+87.84
3	+0.719	+1.59	+2.58	+3.50	+17.66	+39.04	+63.36	+85.94
4	+0.898	+1.88	+2.50	+3.16	+16.55	+34.62	+46.05	+58.20

Table 4. Sodium Tartrate.

No.	α				$[\alpha]_{5461}^{25}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	+0.650	+1.35	+0.72	+0 22	+47.89	+98.0	+53.1	+16.2
2	+1.295	+2.25	+1.36	+0.57	+47.70	+82 9	+50.1	+21.0
3	+1.927	+2.88	+1.96	+1.14	+47.32	+70.8	+48.2	+28.0
4	+2.562	+3.28	+2.63	+1.88	+47.19	+60.5	+46.6	+34.6

Table 5. Potassium Tartrate.

No.	α				$[\alpha]_{5461}^{25}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	+0.625	+1.34	+0.75	+0.26	+46.04	+99.0	+55.3	+19.1
2	+1.280	+2.36	+1.40	+0.66	+47.16	+86.9	+51.6	+24.3
3	+1.989	+2.94	+2.04	+1.17	+48.84	+72.2	+50.0	+28.8
4	+2.722	+3.40	+2.65	+1.96	+50.13	+62.7	+48.8	+36.2

Table 6. Calcium Gluconate.

No.	α				$[\alpha]_D^{25}$			
	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2	H_2O	H_3BO_3	$Na_2B_4O_7$	KBO_2
1	+0.226	+0.544	+0.580	+0.44	+12.64	+30.42	+32.44	+24.61
2	+0.394	+1.13	+1.34	+1.05	+11.02	+31.59	+37.47	+29.36
3	+0.555	+1.64	+2.24	+1.92	+10.35	+30.56	+41.76	+35.80
4	+0.706	+1.99	+2.37	+3.04	+ 9.87	+24.82	+33.09	+42.50

Summary.

By polarimetric observations with regard to the effects of H_3BO_3, $Na_2B_4O_7$ and KBO_2 on various polyoxy compounds the following results and conclusion were obtained.

Boric acid has a very feeble ability for complex formation with non-ionizable polyoxy compounds, such as mannit and glucose, while alkali borates show strong activity upon them. The order of the strengths is $H_3BO_3 \ll Na_2B_4O_7 < KBO_2$. Complex is formed between borate ion and polyhydric alcohols. Its quantity increases with increasing BO_2'.

The effects of boric acid and alkali borates on ionizable polyoxy compounds, like tartaric acid and its salts, appear somewhat complicated. In this case complex formation is possible to a large extent between free boric acid and free tartaric acid (complex I). Complexes are also formed between alkali borate and alkali tartrates (complex II), but they (II) are different in structure from those formed in acidic medium (I). The complex I is formed by the action between BO_2' and alcoholic OH groups, but complex II between $B(OH)_3$ molecule and COO' ion.

Calcium gluconate behaves toward boric acid and borates like alkali tartrates. H_3BO_3 combines with the COO' group of the gluconate, while BO_2' reacts with its alcoholic OH groups.

Thus it has been shown that the complex formation is in general based upon the reaction between molecule and ion, and not between neutral molecules nor between ions.

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